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(54) Water-in-oil-polar solvent emulsions

(57) Water-in-oil-in-non-aqueous polar solvent W/O/PS type multiple emulsion contains a water phase W dispersed in an oil O as the first continuous phase of a primary emulsions W/O by an emulsifier. Primary emulsion W/O is dispersed in a second continuous non-aqueous polar solvent phase PS to form multiple emulsion W/O/PS. The emulsifier is a silicone elastomer containing polyether groups which is a network of polymeric molecules crosslinked with an α,ω-unsaturated hydrocarbon.

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Description

[0001] This invention is directed to water-in-oil-in-polar solvent multiple emulsions W/O/PS in which the polar solvent (PS) is a non-aqueous polar solvent(s).

[0002] Multiple emulsions containing silicone compositions are known in the art. For example, US Patent 5,948,855 (September 7, 1999), discloses certain water-in-oil-in-water ($W_1/O/W_2$) type multiple emulsions. In US Serial No. 09/352,006, filed July 12, 1999, certain oil and water in oil three phase emulsions are described. In US Patent 6,080,394 (June 27, 2000), and US Serial No. 09/498,714, filed February 7, 2000, certain polar solvent-in-oil-in-water ($PS_1/O/W$) type multiple emulsions, as well as certain polar solvent-in-oil-in-polar solvent ($PS_1/O/PS_2$) type multiple emulsions, are described.

[0003] However, none of the prior references disclose a water-in-oil-in-polar solvent (W/O/PS) type multiple emulsion containing a silicone composition, which is the subject matter of the present invention. One advantage offered by a multiple emulsion of the type W/O/PS is that it can be used to isolate active ingredients which are soluble in similar phases from one another. This is particularly applicable when one active ingredient is very soluble in water W, but only marginally soluble in the non-aqueous polar solvent PS, while the other active ingredient is very soluble in PS and marginally soluble in W. Benefits can be most easily attained, however, when the active ingredients are basically insoluble in the oil O, in order to minimize their transport through O.

[0004] Accordingly, the invention relates to a water-in-oil-in-non-aqueous polar solvent W/O/PS type multiple emulsion containing a water phase W dispersed in an oil O as the first continuous phase of primary emulsion W/O by an emulsifier. Primary emulsion W/O is dispersed in a second continuous non-aqueous polar solvent phase PS to form multiple emulsion W/O/PS.

[0005] The emulsifier is (i) a silicone elastomer containing polyether groups which is a network of polymeric molecules crosslinked with an α,ω-unsaturated hydrocarbon; (ii) a silicone elastomer containing acrylate/methacrylate grafted polyether groups which is a network of polymeric molecules crosslinked with an α,ω-unsaturated hydrocarbon; or (iii) a silicone elastomer containing polyether groups and alkyl groups with at least ten carbon atoms which is a network of polymeric molecules crosslinked with an α,ω-unsaturated hydrocarbon. In these emulsifiers, the silicone elastomer contains the continuous oil phase O, preferably a silicone oil, although it may contain other types of oils.

[0006] Emulsifier (i), a silicone elastomer containing polyether groups which is a network of polymeric molecules crosslinked with an α,ω-unsaturated hydrocarbon, can be prepared by methods described in detail in US Patent 5,811,487 (September 22, 1998).

[0007] Generally, such silicone elastomers are prepared by reacting (A) an =Si-H containing polysiloxane; (B) a mono-alkenyl polyether; (C) an α,ω-unsaturated hydrocarbon such as an α,ω-diene, α,ω-diyne, or an α,ω-ene-yne, in the presence of (D) an oil and (E) a platinum catalyst, until a silicone elastomer is formed by crosslinking and addition of =SiH across double or triple bonds in the α,ω-unsaturated hydrocarbon (C).

[0008] Emulsifier (ii), a silicone elastomer containing acrylate/methacrylate grafted polyether groups which is a network of polymeric molecules crosslinked with an α,ω-unsaturated hydrocarbon, can be prepared by methods described in detail in US Patent 5,969,035 (October 19, 1999).

[0009] Generally, such silicone elastomers are prepared by reacting (A) an =Si-H containing polysiloxane; (B) a monoacrylate or monomethacrylate functionalized polyether; (C) an α,ω-unsaturated hydrocarbon such as an α,ω-diene, α,ω-diyne, or an α,ω-ene-yne, in the presence of (D) an oil and (E) a platinum catalyst, until a silicone elastomer is formed by crosslinking and addition of =SiH across double or triple bonds in the α,ω-unsaturated hydrocarbon (C).

[0010] Emulsifier (iii), a silicone elastomer containing polyether groups and alkyl groups with at least ten carbon atoms which is network of polymeric molecules crosslinked with an α,ω-unsaturated hydrocarbon, can be prepared by methods described in detail in US Serial No. 09/352,006, filed July 12, 1999, referred to above.

[0011] Generally, such silicone elastomers are prepared by combining and reacting (A) an =Si-H containing polysiloxane; (B) a mono-alkenyl polyether; (C) an α-olefin containing at least ten carbon atoms; (D) an α,ω-unsaturated hydrocarbon such as an α,ω-diene, α,ω-diyne, or an α,ω-ene-yne, in the presence of (E) an oil, and (F) a platinum catalyst, until a silicone elastomer is formed by crosslinking and addition of =SiH across double or triple bonds in the α,ω-unsaturated hydrocarbon (D).

[0012] The α,ω-unsaturated hydrocarbon can be an α,ω-diene of the formula $CH_2=CH(CH_2)_dCH=CH_2$ where d is 1-20. Some representative examples of suitable α,ω-dienes are 1,4-pentadiene; 1,5-hexadiene; 1,6-heptadiene; 1,7-octadiene; 1,8-nonadiene; 1,9-decadiene; 1,11-dodecadiene; 1,13-tetradecadiene; and 1,19-eicosadiene. Other α,ω-unsaturated hydrocarbons which can be used include α,ω-diynes of the formula $CH{\equiv}C(CH_2)_eC{\equiv}CH$; or α,ω-ene-ynes of the formula $CH_2=CH(CH_2)_eC{\equiv}CH$ where e is 0-20. Some representative examples of suitable α,ω-diynes are 1,3-butadiyne $HC{\equiv}C\text{-}C{\equiv}CH$ and 1,5-hexadiyne (dipropargyl) $HC{\equiv}C\text{-}CH_2CH_2\text{-}C{\equiv}CH$. One example of a suitable α,ω-ene-yne is hexene-5-yne-1 $CH_2=CHCH_2CH_2C{\equiv}CH$.

[0013] US Patents 5,811,487 and 5,889,108 contain extensive lists of appropriate oils which can be used, among which are for example, (i) volatile polydimethylsiloxanes such as hexamethyldisiloxane, octamethyltrisiloxane, and decamethylcyclopentasiloxane, (ii) nonvolatile polydimethylsiloxanes having a viscosity gen-

ally in the range of 5-1,000 centistoke (mm^2/s), (iii) fragrances such as musk and myrrh, and mixtur s th reof.

[0014] Organic oils such as natural oils deriv d from animal, v getable, or mineral sourc s are also suitabl . Most preferred are mod rn cosmetic oils known to be safe for cosmetic purposes such as almond oil, apricot kernel oil, avocado oil, cacao butter (theobroma oil), carrot seed oil, castor oil, citrus seed oil, coconut oil, corn oil, cottonseed oil, cucumber oil, egg oil, jojoba oil, lanolin oil, linseed oil, mineral oil, mink oil, olive oil, palm kernel oil, peach kernel oil, peanut oil, rapeseed oil, safflower oil, sesame oil, shark liver oil, soybean oil, sunflower seed oil, sweet almond oil, tallow (beef) oil, tallow (mutton) oil, turtle oil, vegetable oil, whale oil, and wheat germ oil.

[0015] While the term non-aqueous polar solvent is intended to include solvents generally, when the multiple emulsion is intended for personal care applications, then the non-aqueous polar solvent should be one recognized as being cosmetically acceptable. Representative cosmetically acceptable non-aqueous polar solvents which can be used are monohydroxy alcohols such as ethyl alcohol and isopropyl alcohol; diols and triols such as propylene glycol, 1,2-hexanediol $CH_3(CH_2)_3CH(OH)CH_2OH$, and glycerol; glycerol esters such as glyceryl triacetate (triacetin), glyceryl tripropionate (tripropionin), and glyceryl tributyrate (tributyrin); and polyglycols such as polyethylene glycol. In applications other than personal care, these and other non-aqueous polar solvents can be employed.

[0016] The non-aqueous polar solvent, as well as the water phase, may contain a non-aqueous polar solvent soluble or water soluble active ingredient, respectively, and the oil phase may contain an oil soluble active ingredient.

[0017] Some representative non-aqueous polar solvent soluble active ingredients are (i) non-aqueous polar solvent soluble Vitamins, (ii) non-aqueous polar solvent soluble drugs including activated antiperspirant salts such as aluminum chlorohydrate and aluminum-zirconium trichlorohydrate, or (iii) α-hydroxy acids such as glycolic acid, lactic acid, tartaric acid, and citric acid, i.e., fruit acids.

[0018] US Patent 5,948,855 contains an extensive list of non-aqueous polar solvent soluble and water soluble Vitamins, and non-aqueous polar solvent soluble and water soluble drugs which can be used, among which are Vitamin C, Vitamin B_1, Vitamin B_2, Vitamin B_6, Vitamin B_{12}, niacin, folic acid, biotin, and pantothenic acid. The non-aqueous polar solvent soluble and water soluble vitamin can be used in the multiple emulsion in amounts of from 0.01-50 percent by weight.

[0019] US Patent 5,948,855 also contains an extensive list of oil soluble active ingredients such as vitamins and drugs which can be used in the multiple mulsion, among which ar Vitamin A_1, RETINOL, C_2-C_{18} esters of RETINOL, Vitamin E, TOCOPHEROL, st rs of Vitamin E, RETINYL ACETATE, RETINYL PALMITATE, RETINYL PROPIONATE, α-TOCOPHEROL, TOCOPHERSOLAN, TOCOPHERYL ACETATE, TOCOPHERYL LINOLEATE, TOCOPHERYL NICOTINATE, TOCOPHERYL SUCCINATE, and mixtures thereof. The oil-solubl vitamin or drug can b us d in th multiple emulsion in amounts of from 0.01-50 percent by weight.

[0020] W/O/PS multiple emulsions according to the invention can be prepared by forming a primary emulsion W/O and combining it with a non-aqueous polar solvent PS. For the primary emulsion W/O, it is preferred to use 0.01-99.99 percent by weight of water including the weight of any water soluble active ingredient such as a vitamin which may be carried therein. The oil phase O of the primary emulsion W/O can also comprise 0.01-99.99 percent by weight including the weight of silicone elastomer, oil, and any oil soluble vitamin or active ingredient which may be carried therein. Preferably, the water phase comprises 20-95 percent by weight of the primary emulsion W/O and the oil phase comprises 15-80 percent by weight of the primary emulsion W/O. Multiple emulsions W/O/PS can then be prepared simply by mixing together 0.1-80 percent by weight of primary emulsion W/O and 20-99.9 percent by weight of a non-aqueous polar solvent PS.

Example 1 - Preparation of Primary Emulsion W/O

[0021] 20.8 g of a solution containing 20 percent by weight of a silicone elastomer containing polyether groups in decamethylcyclopentasiloxane, prepared according to the method described in US Patent 5,811,487, in which 9 percent of the repeating units in the backbone are units containing the moiety $-(CH_2CH_2O)_n-$ in which n is 12, were weighed into a glass beaker, and mixed at 800 rpm (84 rad/s) using a mechanical mixer. Over a 5 minute period, 22.9 g of deionized water was added to the beaker and mixed, to form a primary emulsion W/O. In forming the primary emulsion W/O, the silicone elastomer was an emulsifier for water, and the phase O was the silicone elastomer and decamethylcyclopentasiloxane.

Example 2 - Preparation of Multiple Emulsion W/O/PS_1

[0022] 26.0 g of a solution containing one percent by weight of carbomer thickener in propylene glycol (PS_1) was weighted into a glass beaker and mixed at 800 rpm (84 rad/s) using a mechanical mixer. Carbomer is a crosslinked polyacrylic acid polymer sold under the tradename CARBOPOL EDT 2001, by B. F. Goodrich Company, Brecksville, Ohio. 12.0 g of the primary emulsion W/O prepared in Example 1 was added to the beaker and mixed at 1000 rpm (104 rad/s) for 20 minutes. The product was a turbid multiple emulsion that was stable. Examination of th product by optical microscopy confirm d it as multipl mulsion W/O/PS_1.

Example 3 - Preparation of Multiple Emulsion W/O/PS_2

[0023] 22.7 g of a solution containing 3.2 p rc nt by weight of carbom r thickener in 1,2-h xan diol (PS_2) was w ight d into a glass b ak r and mix d at 800 rpm (84 rad/s) using a mechanical mixer. 10.7 g of the primary emulsion W/O prepared in Example 1 was added to the beaker and mixed at 1000 rpm (104 rad/s) for 20 minutes. The product was a turbid multiple emulsion that was stable. Examination of the product by optical microscopy confirmed it as multiple emulsion W/O/PS_2.

[0024] The W/O/PS multiple emulsion is useful in personal care, for example, in preparing antiperspirants and deodorants. It can be used in skin creams, skin care lotions, moisturizers, facial treatments such as acne or wrinkle removers, personal and facial cleansers, bath oils, perfumes, colognes, sachets, sunscreens, preshave and after-shave lotions, shaving soaps, and shaving lathers. It can be used in hair shampoos, hair conditioners, hair sprays, mousses, permanents, depilatories, and cuticle coats. In cosmetics, it can be added to make-ups, color cosmetics, foundations, blushes, lipsticks, eyeliners, mascara, oil removers, color cosmetic removers, and powders. In such applications, it may include oil soluble, polar solvent soluble, and water soluble ingredients such as vitamins as noted above.

[0025] The W/O/PS multiple emulsion is also capable of functioning as a carrier for pharmaceuticals, biocides, herbicides, pesticides, and other biologically active substances; and it has utility as an additive for cellulosic or synthetic nonwoven carrier substrates used in wet-like cleansing wipes such as wet-wipes, tissues, and towels, marketed generally for personal hygiene and household cleaning tasks.

[0026] While the most preferred silicone elastomers for use according to this invention are described in US Patent 5,811,487; US Patent 5,969,035; and US Serial No. 09/352,006, filed July 12, 1999; other silicone elastomers containing polyether groups may be substituted, including silicone elastomers containing polyether groups and higher alkyl groups, provided the performance and benefits are equivalent. Reference may be had, for example, to US Patents 5,889,108 (March 30, 1999) and 5,948,855 (September 7, 1999) for other silicone elastomers considered equivalent.

Claims

1. A composition comprising a water-in-oil-in-non-aqueous polar solvent W/O/PS multiple emulsion including a water phase W dispersed in an oil O first continuous phase of primary emulsion W/O by an emulsifier, the primary emulsion W/O being dispersed in a second continuous non-aqu ous polar solvent phas PS to form multiple mulsion W/O/PS, th emulsifier b ing a silicon elastomer containing poly th r groups which is a n twork of polym ric mol cules crosslink d with an α,ω-unsaturat d hydrocarbon.

2. A composition according to Claim 1 in which th emulsifier is a silicon lastomer containing acrylate/methacrylate grafted polyether groups which is a network of polymeric molecules crosslinked with an α,ω-unsaturated hydrocarbon, or a silicone elastomer containing polyether groups and alkyl groups with at least ten carbon atoms which is a network of polymeric molecules crosslinked with an α,ω-unsaturated hydrocarbon.

3. A composition according to Claim 1 or 2, in which the non-aqueous polar solvent is a monohydroxy alcohol, a diol, a triol, a glycerol ester, or a polyglycol.

4. A composition according to any of Claims 1 to 3, in which the oil is (i) a volatile polydimethylsiloxane, (ii) a nonvolatile polydimethylsiloxane with a viscosity of 5-1,000 centistoke (mm^2/s), (iii) a fragrance, (iv) a natural organic oil derived from an animal, vegetable, or mineral source, or (v) a mixture of two or more oils (1) - (iv).

5. A composition according to any of Claims 1 to 4, in which the non-aqueous polar solvent contains a non-aqueous polar solvent soluble active ingredient selected from

   Vitamins, activated antiperspirant salts, drugs, and α-hydroxy acids; the oil phase contains an oil soluble active ingredient selected from Vitamins and drugs; and the water phase contains a water soluble active ingredient selected from
   Vitamins, activated antiperspirant salts, drugs, and α-hydroxy acids.

6. A composition according to any of Claims 1 to 5, in which the water phase comprises 20-95 percent by weight of the primary emulsion W/O, the oil phase comprises 15-80 percent by weight of the primary emulsion W/O, and the multiple emulsion W/O/PS comprises 0.1-80 percent by weight of primary emulsion W/O and 20-99.9 percent by weight of the non-aqueous polar solvent W.

7. A product containing the composition according to any of Claims 1 to 6, the product being selected from antiperspirants, deodorants, skin creams, skin care lotions, moisturizers, facial treatments, acne removers, wrinkle removers, personal cleansers, facial cleansers, bath oils, perfumes, colognes, sachets, sunscreens, pr -shav lotions, after-shav lotions, shaving soaps, shaving lathers, hair shampoos, hair conditioners, hair sprays, mouss s, p rmanents, d pilatories, cuticle coats, make-up, color

cosm tics, foundations, blush s, lipsticks, ey lin- rs, mascara, oil r movers, color cosm tic remov- rs, bath powd rs, body powders, pharmaceuticals, biocid s, herbicides, p sticid s, biologically active substances, cellulosic substrates, synthetic nonwoven substrates, wet-cleansing wipes, tissues, and towels.

8. A method of treating hair, skin, or underarm, comprising applying to hair, skin, or underarm the composition according to any of claims 1 to 6.

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EUROPEAN SEARCH REPORT

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	27 November 2001	De La Morinerie, B

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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